



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of

Forestiere et al

Examiner: J. W. Pasterczyk

Serial No.: 09/864,877

Group Art Unit: 1755

Filed: May 25, 2001

For: MATERIALS COMPRISING ORGANIC GROUPS CONTAINING SULPHUR AND PHOSPHOROUS BONDED TO A MINERAL OXIDE VIA OXYGEN ATOMS

DECLARATION UNDER RULE 37 C.F.R. § 1.132

Assistant Commissioner for Patents

Washington, D.C. 20231

SIR:

I, Germain Martino, duly warned, declare and say as follows:

THAT, I am a French citizen; that I graduated from "Faculté des Sciences de l'Université de Strasbourg" (France) in 1961; that I obtained an Engineer Diploma from "Ecole Nationale Supérieure de Pétrole et des Moteurs" Rueil-Malmaison (France) in 1963; that I was received as a Doctor by "Université de Louvain" (Belgium) in 1965; and that I now reside in 78300 Poissy (France), 80 avenue Fernand-Lefebvre;

THAT, I was hired by "Institut Français du Pétrole" Rueil-Malmaison (France) in their Research Department to research on catalytic agents and catalytic reactions in May 1967; that, from January 1985 to September 1989, I was Manager of the Kinetics and Catalysis Research Division; that, from September 1989 to December 1997, I was Assistant Manager of the whole Refining and Petrochemical Technology Business Unit; and that since then I have been Manager of said Refining and Petrochemical Technology Business Unit.

I declare further:

THAT, I am familiar with the contents of U.S. Patent Application Serial No. 09/864,877, which relates to MATERIALS COMPRISING ORGANIC GROUPS CONTAINING SULPHUR AND PHOSPHOROUS BONDED TO A MINERAL OXIDE VIA OXYGEN ATOMS.

THAT, I am aware of the teachings of U.S. Patent 4.994.429 cited by the Examiner in his Office Action of November 14, 2003.

THAT in order to support patentability of the present application, I have carried out the following comparative experiment.

Example 3 (not in accordance with the invention : Material according to Wieserman synthesis)

In the example we reproduced the synthesis process described in US 4,994,429 to prepare a functionalized solid comprising a sulfonic acid group.

We carried out according the preparative mode described in example 2 of Wieserman. 10 grams (125.2 millimoles) of titanium dioxide P25 Degussa was mixed with 139,1 ml of a solution 0,3M of phenylphosphonic acid. The mixture was shaken at 60°C for 1 hour. The resulting solid was then dried at 110°C for 12 hours. 5 grams of this functionalized solid was placed in a 100 ml drum together with 10ml of fuming sulfuric acid. The drum was capped and swirled to coat the particles. The mixture was then mechanically shaken for 90 seconds. The contents was then placed in 1.5 liter of deionized water and allowed to settle. After filtration, the solid was washed three times with 1.5 liters of deionized water each time. The water was then decanted off and the contents were covered with methanol. The product was allowed to settle overnight and the methanol was then decanted off after which the product was then again covered with methanol which was allowed to evaporate off. The product was then in a vacuum oven overnight at 60°C.

Elemental analysis of the resulting solid gave the following results : Ti : 55%, P : 0.4%; S: 0.53%. The Ti/P ratio was 90 and the S/P ratio was 1,3.

A substantial part of the phosphonate group is then generated by this kind of synthesis process.

The phosphorous-31 NMR spectrum of the solid carried out using a 300MHz Bruker Avance Apparatus, illustrated by the following figure1, shows a sharp peak at -4.3 ppm corresponding to phenylphosphonate groups bonded to titanium atoms in a multilayer such as set forth in the instant specification page 1 line 25 and a broad peak at 13,9 ppm corresponding to phenylphosphonate group bonded to the surface of the titanium dioxide particles.

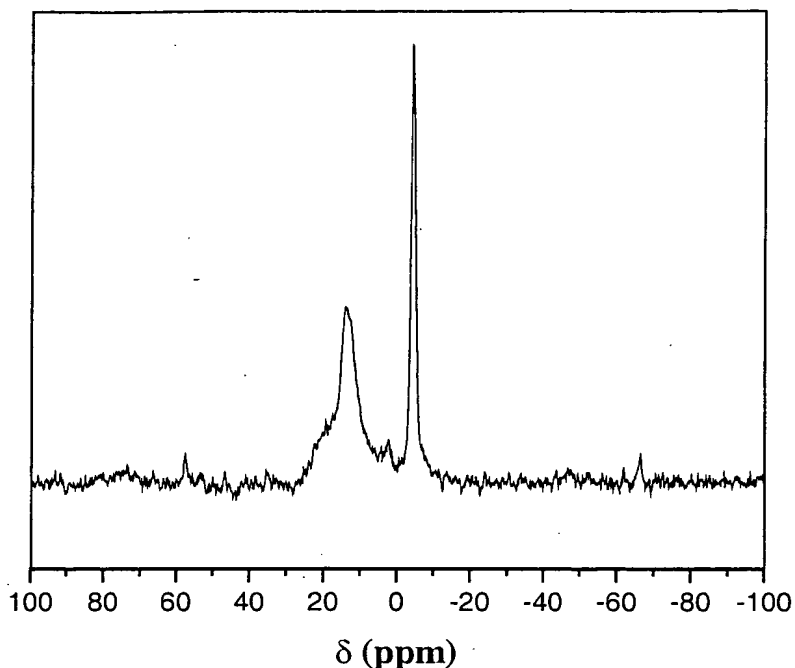


Figure 1

Example 4 (in accordance with the invention)

In a Schlenk tube with a argon gas circulation, 0.752 gram (3.16 millimoles) of sulfophenylphosphonic acid was solved in 15.1 ml of isopropanol. 4.49 grams (15.8 millimoles) of tetraisopropoxytitanate was added until the final concentration of the metallic alcocide is 0,8 mole/l.

The mixture was shaken for two hours in the presence of argon gas and 0.51 gram of dionized water was added in a drip for a one hour time limit. The gel formation occurred and the gel was kept two days as it was for maturation. The resulting solid was crushed and washed with isopropanol, then washed successively with ethanol, acetone, and ether before being vacuum dried at 120°C under a pressure of 0.1 millibar for five hours.

Elemental analysis of the resulting solid gave the following results : Ti : 38.8%, P : 4.86%; S: 5.28%. The Ti/P ratio was 5.6 and the S/P ratio was 1,1.

The phosphorous-31 NMR spectrum of the solid carried out using a 300MHz Bruker Avance Apparatus, illustrated by the following figure 2, shows a single broad peak at 11.3 ppm attributed to phénylphosphonate group bonded to the surface of the particles.

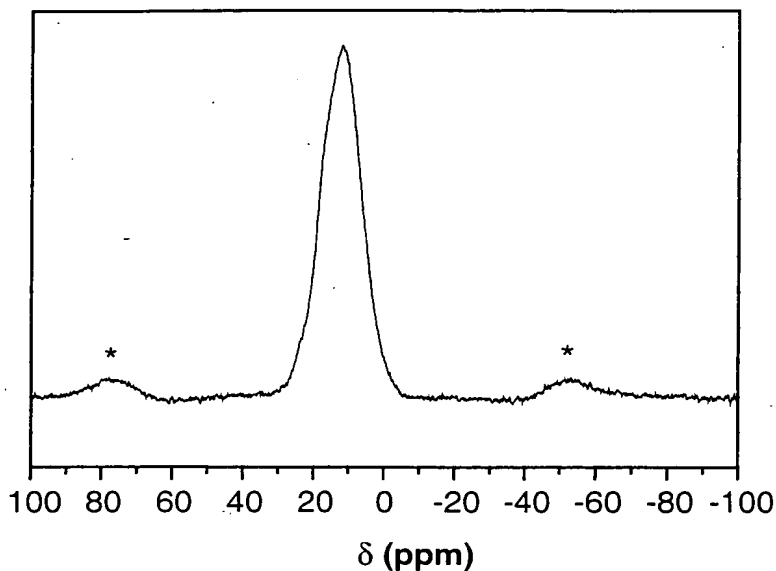


Figure 2

The synthesis by acid attack according to Wieserman do not generate a single phase but a mixture of the functionalized material and aluminium phosphonate as by-product. This is a major drawback. Our gel formation method leads to a single, pure product which chemical nature is different, i. e. wherein at the same time M-O-P or M-O-M are distributed both at the surface or in the bulk of the final particle.

The undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information or belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Germain Martino

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Date: January 28, 2003